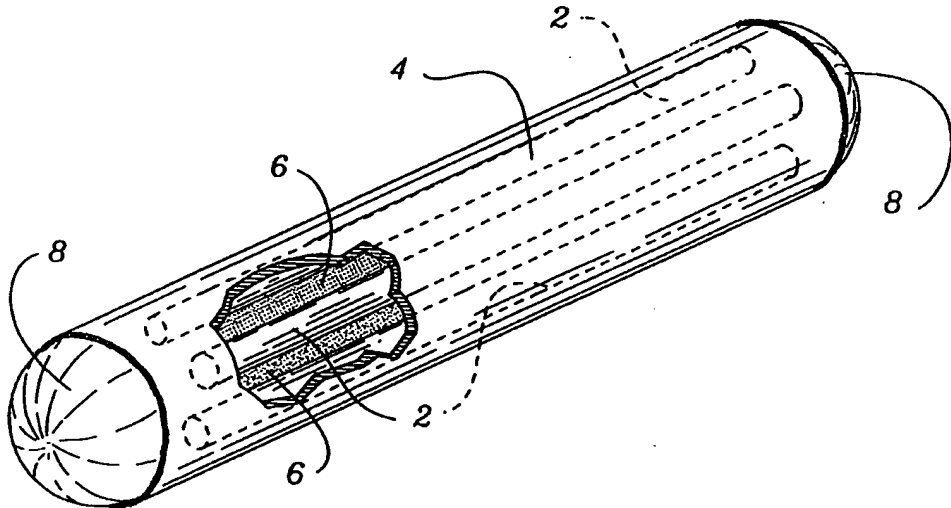


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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>C23C 10/52</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/20182</b> <b>(43) International Publication Date:</b> 14 May 1998 (14.05.98)
<b>(21) International Application Number:</b> PCT/US97/15857 <b>(22) International Filing Date:</b> 7 November 1997 (07.11.97)  <b>(30) Priority Data:</b> 08/745,199 8 November 1996 (08.11.96) US  <b>(71) Applicant:</b> ALON, INC. [US/US]; Grantham Street, P.O. Box 231, Tarentum, PA 15084 (US).  <b>(72) Inventors:</b> BAYER, George, T.; 416 West 7th Avenue, Tarentum, PA 15084 (US). WYNNS, Kim, A.; 8026 Downingtown Court, Spring, TX 77379 (US).  <b>(74) Agent:</b> ALSTADT, Lynn, J.; 20th floor, One Oxford Centre, 301 Grant Street, Pittsburgh, PA 15219-1410 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> ALUMINUM-SILICON DIFFUSION COATING		
		
<b>(57) Abstract</b>  A method of forming an aluminum-silicon diffusion coating on a surface of an alloy product utilizes a pack mixture containing by weight 1 % to 5 % aluminum, 0.5 % to 5 % silicon, 0.25 % to 3 % ammonium halide activator and the balance an inert filler. The product to be coated is placed in a retort with the pack mixture covering the product surfaces to be coated. Upon heating aluminum and silicon will diffuse onto the product surfaces forming the aluminum-silicon diffusion coating.		

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## TITLE

### ALUMINUM-SILICON DIFFUSION COATING

## FIELD OF INVENTION

The invention relates to a method of diffusion coating an iron, nickel, cobalt, or copper base alloy with an aluminum-silicon containing coating diffused onto the surface of alloys using a pack cementation process and the insert used in that process.

## BACKGROUND OF THE INVENTION

Pack cementation is a well known technique for applying diffusion coatings to metal surfaces. This process involves placing a pack mixture into close contact with the surface being coated and subsequently heating the entire assembly to an elevated temperature for a specified period of time. During heating the coating material diffuses from the pack onto the surface of the metal by a combination of chemical reactions and gas phase mass transport. Pack cementation is commonly used to apply aluminum diffusion coatings as well as to apply chromium diffusion coatings. A common pack mixture used to create a chromium coating contains chromium, an inert filler such as alumina, and a halide activator. Similarly a common pack mixture used to produce an aluminum coating consists of an aluminum source, a halide salt activator and an inert diluent or filler such as alumina. Davis in United States Patent No. 4,904,501 teaches that ammonium chloride, sodium chloride and ammonium bromide can be used as activators.

Aluminum-silicon diffusion coatings are preferred over aluminum diffusion coatings for some applications because silicon in the coating improves hot corrosion and ash corrosion resistance and reduces brittleness of the coating. The art has developed several methods of applying an aluminum-silicon coating to ferrous metal articles. Most commercial processes that are used to apply aluminum-silicon diffusion coatings require separate diffusion steps for each element or use expensive masteralloys. Masteralloys of aluminum and silicon cost 3 to 4 times more than pure aluminum and twice as much as pure silicon on a weight basis. Consequently, those skilled in the art have been searching for a less expensive process, particularly one in which an aluminum-silicon diffusion coating is applied in a single step. Preferably, the process should not require any materials that are expensive or difficult to obtain. The process should be suitable for use on existing equipment and for large scale processing operations. Both United States Patent No. 4,500,364 and No. 4,310,574 discloses processes in which a slurry coating is applied to the article followed by high temperature firing. Slurries are more difficult to handle than the more common powder mixtures used in most pack cementation processes.

Krutenat in United States Patent No. 4,500,364 discloses an aluminum-silicon slurry containing from 0.5 to 2.0% by weight sodium chloride activator. As will be seen from data presented herein, the coating thickness produced using this mix never exceeded 180 microns (7 mils) and was as thin as 80 microns (3 mils). Coatings this thin are not acceptable for many industrial applications. The petrochemical/chemical processing industry, for example, often demand coating thickness of 250 microns (10 mils) or more.

Japanese Patent application 54090030 discloses a process in which steel plate is buried in an agent comprised of aluminum powder, silica ( $\text{SiO}_2$ ) powder and a halide and then heated at  $1000^\circ\text{C}$ . in a nonoxidizing atmosphere to apply an aluminum and silicon diffusion coating. Because of the low reactivity of the silica powder, the resulting coating would contain very little silicon. Therefore, the benefits of having silicon in an aluminum diffusion coating are not obtained.

### SUMMARY OF THE INVENTION

We provide a method of diffusion coating iron-, nickel-, cobalt- and copper-based alloys by simultaneous deposition of aluminum and silicon coating using a pack mix containing pure aluminum, pure silicon and an ammonium halide activator. The components to be coated are placed in a carbon steel or high temperature alloy retort and the surfaces to be coated are covered by the pack mix. The retort may be heated to between  $150^\circ$  to  $200^\circ\text{C}$ . ( $300^\circ$  to  $400^\circ\text{F}$ .) for one hour or longer to remove any oxygen or moisture present. Then the retort is heated to an interior temperature of  $650^\circ$  to  $1150^\circ\text{C}$ . ( $1200^\circ$  to  $2100^\circ\text{F}$ .) and held at that temperature for a selected time period. That time period will depend upon the base alloy being coated and the required depth of the diffusion coating. After the selected heating period has passed the retort is rapidly cooled and opened. Then the aluminum-silicon diffusion coated parts are removed. The coated parts are then cleaned and, if desired, also abrasive blasted.

### BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a perspective view of a retort partially cut away which contains tubular products and our pack for applying an aluminum-silicon diffusion coating in accordance with a first preferred embodiment of our method; and

Figure 2 is a perspective view similar to Figure 1 of a retort partially cut away which contains tubular products and our pack for applying an aluminum silicon-diffusion coating in accordance with a second preferred embodiment of our method.

Figure 3 is a perspective view similar to Figure 1 where a pack mix with added binder is contained in a composite ceramic sheet placed adjacent to surfaces of plates to be coated.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

We provide a method of applying an aluminum-silicon diffusion coating on a surface of a workpiece formed from an iron-, nickel-, cobalt- or copper-based alloy by simultaneous deposition of aluminum-silicon coating using a pack mix containing pure aluminum, pure silicon and an ammonium halide activator. Our method could be used to coat both sheet and tubular stock as well as complex shapes or parts. In Figures 1 and 2 we illustrate the method being used to coat tubes. The components 2 to be coated are placed in a carbon steel or high temperature alloy retort 4 and are surrounded by the pack mix 6. In Figure 1, the pack mix is a powder which has been packed inside and around the tubes 2 filling the retort 4. The ends of the retort are closed by lids 8 which may be welded or hermetically sealed. It should be understood that the retort typically will have a cooling jacket, associated piping and vents not shown in the Figures. No introduced atmosphere is necessary. However, argon or argon-hydrogen

mixtures can be used as a purge gas to provide an inert or reducing atmosphere. The retort may be first heated to between 150° to 200°C. (300° to 400°F.) for one hour or longer to remove any oxygen or moisture present. Then the retort is heated to an interior temperature of 650° to 1150°C. (1200° to 2100°F.) and held at that temperature for a selected time period. That time period should range from 5 to 45 hours and will depend upon the base alloy being coated and the required depth of the diffusion coating. After the selected heating period has passed the retort is rapidly cooled and opened. Then the aluminum-silicon diffusion coated parts are removed. The coated parts are then cleaned and, if desired, also abrasive blasted.

In the first preferred embodiment of our method illustrated by Figure 1 we fill the retort with pack mix to surround the products being coated. The pack mix contains 1-5 % aluminum, 0.5-5% silicon, 0.25-3% ammonium halide activator by weight and the balance being an inert filler such as aluminum oxide. Suitable activators are ammonium fluoride, ammonium chloride, ammonium bromide and ammonium iodide. The components being coated must be free of all dirt, oil, grease, paint, rust and mill scale. In the illustrated process the tubes 2 are filled with and surrounded by pack mix to provide a diffusion coating on both the inner walls and outer walls. When only the inside surface of tubes, complex shapes or parts are to be diffusion coated, it is possible to fill the tubes or other workpieces with pack mix covering only the inside surfaces. The pack mix is held in place by metal caps or an adhesive tape. The packed tubes or other workpieces can then be loaded into an empty retort and processing will be performed as described above. Since powder is only present in the tubes or other workpieces, improved heat transfer to them will be achieved. The product to be coated can be of any desired length and may include both straight portions and return bends.

### **EXAMPLE 1**

Type 1018 carbon steel, type 304 austenitic stainless steel, and Alloy 800 (iron-base superalloy) samples were simultaneously diffusion coated with aluminum-silicon in a pack cementation process. The pack composition consisted of 4 wt.% aluminum, 0.5 wt.% silicon, 0.5 wt.% ammonium chloride, and 95 wt.% aluminum oxide. The process was conducted in a hermetically sealed carbon steel retort. The process consisted of heating the retort in a furnace at a temperature ranging from 1500°F - 1800°F for 5 hours.

The diffusion coated samples were examined by standard metallographic techniques. The type 1018 carbon steel sample exhibited an average diffusion zone thickness of approximately 300 microns with no porosity and minimal grain boundary formation running perpendicular to the diffusion zone surface. Scanning electron microscopy/energy dispersive spectrometric measurements indicated a composition including 36.7 wt.% aluminum and 0.3 wt.% silicon at the diffusion zone surface. The type 304 austenitic stainless steel sample exhibited an average diffusion zone thickness of approximately 300 microns with no grain boundary formation and no porosity. The Alloy 800 sample exhibited an average diffusion zone thickness of 100 microns with no grain boundary formation and no porosity.

### **EXAMPLE 2**

Samples of a 98 wt.% copper - 2 wt.% beryllium alloy were simultaneously diffusion coated with aluminum-silicon in a pack cementation process. The pack composition consisted of 4 wt.% aluminum, 1 wt.% silicon, 1.5 wt.% ammonium chloride, and 93.5 wt.% aluminum oxide. The process was conducted in a



hermetically sealed carbon steel retort. The process consisted of heating the retort in a furnace at a temperature ranging from 1470°F - 1500° for 5 hours.

The diffusion coated samples were examined by standard metallographic techniques. The copper-beryllium samples exhibited an average diffusion zone thickness of approximately 150 microns, ranging between 100 and 200 microns, with no porosity and minimal grain boundary formation running perpendicular to the diffusion zone surface. As this alloy is used for an erosive/wear environment, hardness measurements of the diffusion zone surface were obtained. The average hardness of the diffusion zone surface was found to be 66 on the Rockwell C scale.

It is not necessary to completely fill the retort with workpieces and pack mix. As shown in Figure 2, the items 12 to be coated are much shorter than the retort 4. Consequently, the products 12 are placed in one end of the retort 4 and surrounded with pack mix 6. A protective ceramic fiber sheet 14 is placed on the top of the pack mix while the balance of the retort remains empty. The ceramic fiber sheet 14 holds the pack mix 6 in place during heating. The heating process is preferably performed in the same manner as was described for the first embodiment. An inert or reducing gas is introduced into the space 16 above the pack mix 6 and ceramic fiber sheet 14. Since less pack mix is used than in a fully packed retort, improved heat transfer to the pack components will be achieved.

In a third embodiment shown in Figure 3 we provide a composite pack-mix binder sheet 20 containing the proper proportions of aluminum, silicon, ammonium halide, aluminum oxide and binder. This sheet 20 is laid in the retort 4 adjacent to the plates or other components 22 to be coated. Then the retort is heated. Aluminum and silicon diffuse from the composite sheet 20 onto surfaces of plates 22 adjacent to the

composite sheet 20 and the parts are further processed as described in the first embodiment.

If it is desired to coat only the inner surfaces of tubes or other hollow structure, one can use a composite insert containing the proper proportions of aluminum, silicon, ammonium halide, aluminum oxide and binder. The insert is placed into the tubes or other hollow structure whose inner walls are to be coated. The items containing inserts are capped or taped and loaded in a retort. The retort is heated as previously described to create a diffusion coating on the inner walls of the tubes or other hollow structure in the retort. Thereafter, the tubes are removed from the retort and the insert is removed from the tubes. The tubes can then be cleaned, abrasive blasted or subjected to other treatments. The use of such composite insert should provide faster heating of the items to be coated. Also, the insert and coated articles cool faster than a retort which is completely filled with powder as illustrated in Figure 1. We have observed that a non-uniform temperature distribution can occur in the components in a retort packed as in Figure 1. Use of an insert should minimize the effects of this condition.

We tested aluminum-silicon diffusion coatings for carbon steel pipe to compare the coatings produced when ammonium chloride is used as an activator with coatings produced when sodium chloride is used. We selected the percentage of activator as 0.5% or 2.0% to correspond to the limits disclosed and claimed by Krutenat in United States Patent No. 4,500,364.

All experiments were conducted in a carbon steel retort containing ASTM A 53, 1" IPS schedule 80 carbon steel pipe with the powder mix packed on the ID surfaces and with an inert argon atmosphere provided in the retort. Each mix was

contained in one separate pipe with caps tack welded to both ends. All pipes were heated together. The heating cycle consisted of heatup of the retort in a gas fired furnace to 1800°F. for twelve (12) hours, followed by as rapid a cooling cycle as possible. Two specimens were cut from each tube, mounted, and polished according to standard metallographic procedures. Coating depths were measured and the specimens were subjected to scanning electron microscopy/energy dispersive spectrometry to determine surface aluminum and silicon composition of the diffusion coatings. The data for the two specimens was arranged to give results for each sample.

The results of these experiments are shown in Table I. The even number samples correspond to Krutenat while the odd numbered samples embody the present invention:

**TABLE I**

Sample	Mix Composition (wt.%)	Temp.(F)	Time (hrs.)	Diffusion (microns)	Surface Al-Si(wt.%)
1	5Al, 1 Si 0.5 NH <sub>4</sub> Cl	1800	12	200-230	16.7-2.5
2	5 Al, 1 Si, 0.5 NaCl	1800	12	150-180	9.6-1.8
3	1 Al, 5 Si 0.5 NH <sub>4</sub> Cl	1800	12	100-130	6.7-2.0
4	1 Al, 5 Si, 0.5 NaCl	1800	12	80-100	7.2-2.7
5	1 Al, 5 Si 2 NH <sub>4</sub> Cl	1800	12	130-150	4.9-1.8
6	1 Al, 5 Si 2 NaCl	1800	12	80-100	6.4-0.8
7	5 Al, 5 Si 0.5 NH <sub>4</sub> Cl	1800	12	250-280	20.2-3.4

8	5 Al, 5 Si, 0.5 NaCl	1800	12	150-180	13.1-2.2
9	5 Al, 5 Si, 2 NH <sub>4</sub> Cl	1800	12	280-300	23.6-1.6
10	5 Al, 5 Si, 2 NaCl	1800	12	150-180	9.8-2.2

It is apparent from the data in Table 1 that the pack mix containing ammonium chloride consistently produced thicker coatings. More importantly, none of the mixes containing sodium chloride produced a coating of at least 250 microns. Hence, these mixes could not be used to coat parts for the petrochemical/chemical processing industry which often demands coatings of at least 250 microns. Ammonium chloride does provide an aluminum-silicon diffusion coating having the industry's desired diffusion coating thicknesses and surface aluminum-silicon concentrations when the mix contained 5% aluminum and 5% silicon. At this level of aluminum and silicon, the activator could be from 0.5 to 2% by weight and the mix will produce the desired coating thickness. Furthermore, the aluminum content in the coating was much greater. Sample 1 having 5% aluminum and 1% silicon produced a coating thickness of 200-230 microns. Thus, the data indicates that the preferred pack mixes will contain at least 5% aluminum.

While we have described and illustrated certain present preferred embodiments of our pack mix and methods for applying an aluminum-silicon diffusion coating, it should be distinctly understood that our invention is not limited thereto, but may be variously embodied within the scope of following claims.

We claim:

1. A method of coating a surface of an alloy product comprising:
  - a. preparing a diffusion mixture consisting essentially of by weight 1% to 5% aluminum, 0.5% to 5% silicon, 0.25% to 3% ammonium halide activator and the balance an inert filler;
  - b. placing the diffusion mixture in a retort with the alloy product to be coated so that the diffusion mixture covers those surfaces of the product which are to be coated; and
  - c. heating the retort to a sufficiently high temperature to cause aluminum and silicon in the mixture to diffuse onto at least one surface of the alloy product forming an aluminum silicon coating.
2. The method of claim 1 wherein the retort is heated to an interior temperature of from 650° to 1150°C.
3. The method of claim 2 also comprising the step of injecting argon gas into the retort.
4. The method of claim 3 also comprising the step of injecting hydrogen with the argon gas into the retort.
5. The method of claim 1 wherein the coating is applied by surface chemical diffusion from at least one of a composite pack mix-binder sheet and a composite pack mix-binder insert which contains the diffusion mixture.

6. The method of claim 1 wherein the activator is selected from the group consisting of ammonium fluoride, ammonium chloride, ammonium bromide, and ammonium iodide.

7. The method of claim 1 wherein the diffusion mixture fills only a portion of the retort.

8. The method of claim 1 wherein the diffusion mix contains at least 5% by weight of aluminum and at least 0.5% by weight of ammonium chloride.

9. The method of claim 7 wherein the diffusion mixture is a powder.

10. The method of claim 1 wherein the inert filler is aluminum oxide.

11. A metal alloy product having an aluminum-silicon diffusion coating on at least one surface, the aluminum and silicon diffusion coating being formed by the steps of:

- a. preparing a diffusion mixture consisting essentially of by weight 1% to 5% aluminum, 0.5% to 5% silicon, 0.25% to 3% ammonium halide activator and the balance an inert filler;
- b. placing the diffusion mixture in a retort with the alloy product to be coated so that the diffusion mixture covers those surfaces of the product which are to be coated; and
- c. heating the retort to a sufficiently high temperature to cause aluminum and silicon in the mixture to diffuse onto at least

one surface of the alloy product forming an aluminum-silicon coating.

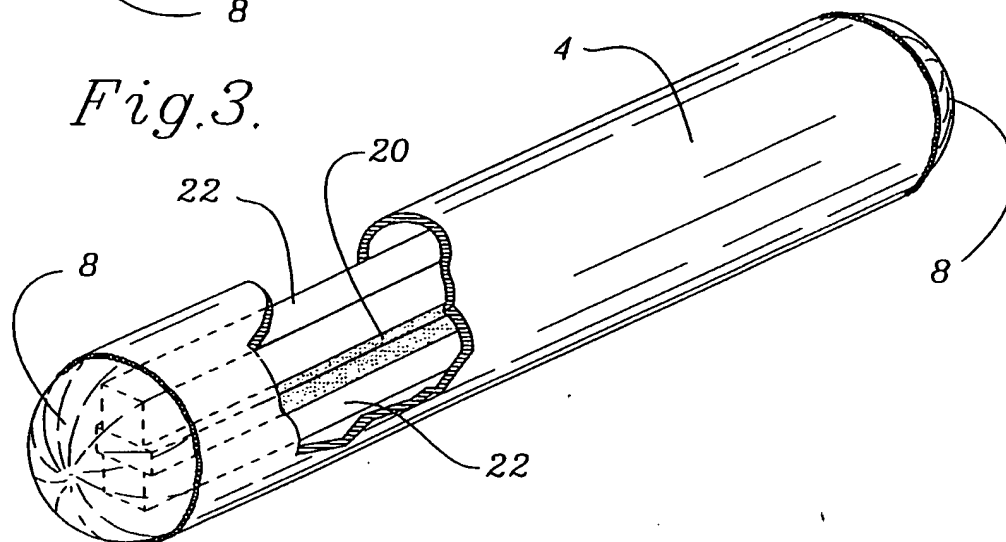
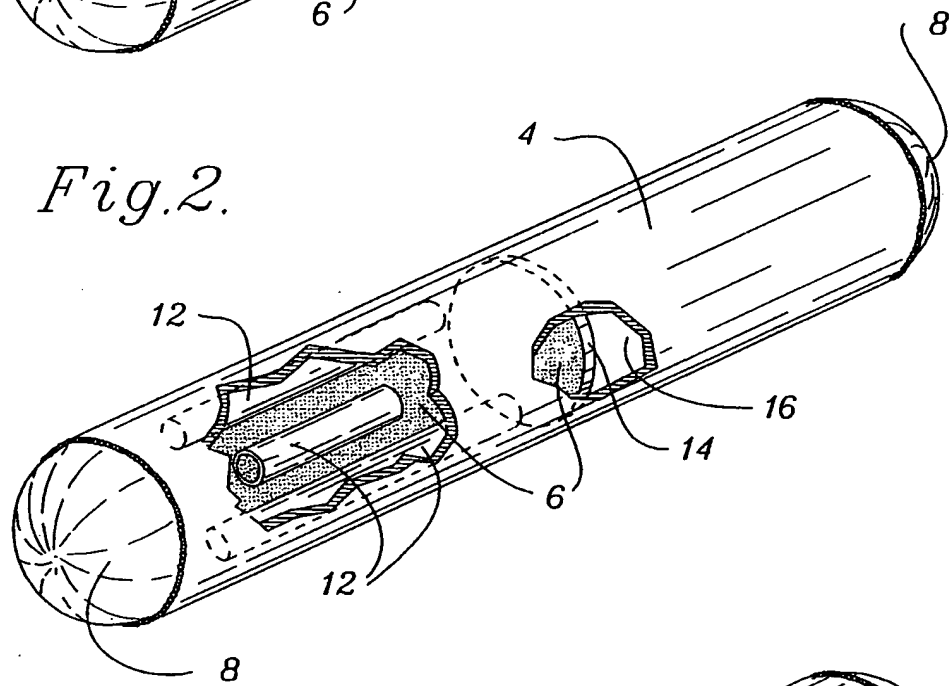
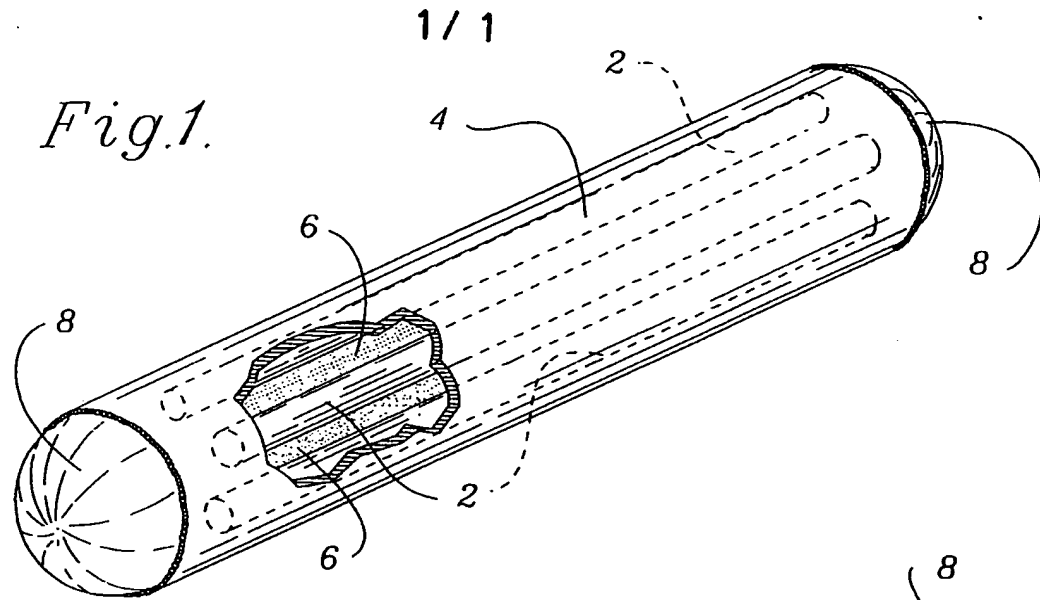
12. The metal alloy product of claim 11 wherein the activator is selected from the group consisting of ammonium fluoride, ammonium chloride, ammonium bromide, and ammonium iodide.

13. The metal alloy product of claim 11 wherein the coating is applied by surface chemical vapor diffusion from at least one of a pack mix-binder composite sheet and a composite pack mix-binder insert which contains the pack mixture.

14. The metal alloy product of claim 11 wherein the activator is selected from the group consisting of ammonium fluoride, ammonium chloride, ammonium bromide, and ammonium iodide.

15. The metal alloy of claim 11 wherein the aluminum-silicon diffusion coating has a thickness of at least 250 microns.

16. The metal alloy product of claim 11 wherein the diffusion mix contains at least 5% by weight aluminum and at least 0.5% ammonium chloride.





# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/15857

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C23C10/52

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 004, no. 129 (C-024), 10 September 1980 & JP 55 082768 A (HITACHI LTD), 21 June 1980, see abstract	1,2,6, 8-12,16
Y	EP 0 184 354 A (THE SECRETARY STATE FOR DEFENCES IN HER BRITANNIC MAJESTY'S GOVERNEMENT) 11 June 1986	1,2,6, 8-12,16
A	see claims 13,4,5,6,14; example 1 --- -/--	3,7

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 8606 Derwent Publications Ltd., London, GB; Class M13, AN 86-041448 XP002058978 &amp; SU 1 168 626 A (ARAKELIAN V S) , 23 July 1985 see abstract</p>	1,2,6, 8-12
A	<p>EP 0 294 987 A (EXXON RESEARCH AND ENGINEERING COMPANY) 14 December 1988 see claims 1,2,9,10</p>	1,11
A	<p>FR 2 030 314 A (UNITED AIRCRAFT CORPORATION) 13 November 1970 see claims 1,3</p>	1,2,6, 8-12
A	<p>FR 1 377 238 A (DEUTSCHE EDELSTAHLWERKE) 15 February 1965 see page 2, column 2, line 5 - line 9; claims 1,2C</p>	1,2,6, 8-12
A	<p>US 2 097 024 A (WALTER ENDERS) 26 October 1937 see page 1, line 26 - line 31; claims 1-5</p>	1,2,11
A	<p>B.S. KUKHAREV: "effect of diffusional aluminum siliciding on the oxidation resistance of carbon steels" METAL SCIENCE AND HEAT TREATMENT, vol. 25, no. 5/6, May 1983 - June 1983, NEW-YORK,US, page 357 XP002058977</p>	1,2,6, 8-12
A	<p>FR 2 511 396 A (ELECTRICITE DE FRANCE) 18 February 1983</p>	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

PCT/US 97/15857

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 184354 A	11-06-86	GB 2167773 A	04-06-86
		CA 1263571 A	05-12-89
		DE 3564290 A	15-09-88
		US 4687684 A	18-08-87
EP 294987 A	14-12-88	US 4835010 A	30-05-89
		CA 1324918 A	07-12-93
		DE 3883857 D	14-10-93
		DE 3883857 T	05-01-94
		JP 1056861 A	03-03-89
		JP 2567456 B	25-12-96
FR 2030314 A	13-11-70	BE 745536 A	16-07-70
		CH 538550 A	15-08-73
		DE 2003480 A	15-10-70
		GB 1274821 A	17-05-72
		NL 7001617 A	07-08-70
		SE 361685 B	12-11-73
		ZA 7000543 A	27-01-71
FR 1377238 A	15-02-65	NONE	
US 2097024 A	26-10-37	NONE	
FR 2511396 A	18-02-83	NONE	